



This application is based on German Application No. 102 52 607.9, which was filed on November 12, 2002.

5           The invention relates to a process for producing a nanoelement arrangement  
and to a nanoelement arrangement.

With ongoing miniaturization, conventional silicon microelectronics will reach its limit. Disruptive short-channel effects are becoming an ever more important factor with ongoing miniaturization in a field-effect transistor, restricting the conductivity of the field-effect transistor. In addition to the problems which arise in an individual component, a further difficulty in a memory arrangement is a limited scalability of the storage medium, for example the capacitance in a DRAM (dynamic random access memory) cannot be scaled to any desired degree.

The use of carbon nanotubes is under discussion as a possible successor technology to silicon microelectronics. Basic principles of carbon nanotubes are described, for example, in Harris, PJF (1999) "Carbon Nanotubes and Related Structures - New Materials for the Twenty-first Century", Cambridge University Press, Cambridge, pp. 1 to 15, 111 to 155. It is known that carbon nanotubes (depending on the tube parameters) have an electrical conductivity ranging from semiconducting to metallic.



nanotubes using a CVD process starting from the iron clusters which have a catalytic action for the growth of carbon nanotubes. The diameter of the carbon nanotubes can be set by predetermining the diameter of the clusters.

Murray, CB, Sun, S, Doyle, H, Betley, T "Monodispersive 3d Transition-Metal (Co, Ni, Fe) Nanoparticles and Their Assembly into Nanoparticle Superlattices", MRS Bulletin, December 2001, discloses a process by which metal clusters can be produced from 3d transition metals.

Cao, A, Zhang, X, Xu, C, Liang, J, Wu, D, Wei, B (2000) "Carbon nanotube dendrites: Availability and their growth model", Materials Research Bulletin 36:2519-2523, discloses a growth model for dendrites of carbon nanotubes.

Sun, LF, Liu, ZQ, Ma, VC, Tang, DS, Zhou, WY, Zou, XP, Li, YB, Lin, JY, Tan, KL, Xie, SS (2001) "Growth of nanofibers array under magnetic force by chemical vapor deposition", Chemical Physics Letters 336:392-396, discloses the growth of carbon nanofibres under magnetic force by means of a CVD process.

Zhu, H, Ci, L, Xu, C, Liang, J, Wu, D (2002) "Growth mechanism of Y-junction carbon nanotubes", Diamond and Related Materials 11:1349-1352, discloses a growth mechanism of Y-junction carbon nanotubes.

The invention is based on the problem of providing a different process for producing a nanoelement arrangement and a different nanoelement arrangement in which it is possible to predetermine whether nanoelements are branched.

A first nanoelement, which has already been fully produced, is at least partially covered with catalyst material for catalyzing the growth of nanoelements in the process for producing a nanoelement arrangement. Then, at least one second nanoelement is grown on the catalyst material.

A basic idea of the invention is for one location or a plurality of locations on the first nanoelement, on which at least one second nanoelement can preferentially be grown, is or are predeterminable by covering partial regions, which can be predetermined in a defined manner, of a first nanoelement which has already been  
20 fully produced. These locations can be predetermined by the catalyst material being deposited in targeted fashion on desired regions of the first nanoelement. Since the catalyst material has a catalytic action for the growth of nanoelements, in a subsequent process step for forming second nanoelements, the second nanoelements grow

preferentially on the catalyst regions on the first nanoelement. Since it is technologically feasible to produce clusters from 3d transition metals with a targeted dimension in the nanometre range, and since numerous 3d transition metals (e.g., iron, cobalt, nickel), for example, catalytically promote the formation of carbon nanotubes, highly accurate definition of growth locations for second nanoelements on the surface of a first nanoelement is possible.

According to the invention, there is no need for a substrate to produce branched networks of nanoelements.

Furthermore, complex multiple branching of nanoelements according to the  
10 requirements of a particular application, e.g., of an integrated circuit with branched  
interconnects, are possible.

The invention is based on the experimental discovery that catalyst material, for example in the form of metallic clusters, bonds particularly well to nanoelements, such as for example carbon nanotubes, creating a reliable way of predetermining the locations of the subsequent growth of a second nanoelement and of ensuring permanent bonding of the catalyst material. By way of example, a cobalt cluster may be surrounded by a monolayer of an organic material, which monolayer has a good bonding action with carbon nanotubes.

Since catalyst material for the growth of nanoelements in many cases has a  
20 good electrical conductivity (for example 3d transition metals, such as iron, cobalt or  
nickel), an electrically conductive coupling location between the nanotubes is  
possible. It is therefore possible to produce a continuous conductive connection





other words, the material of the protective layer is preferably selected in such a way that nanoelements cannot grow or can only grow to a slight extent on the protective layer. In such a case, significant growth of nanoelements is only possible where the first nanoelement does not have the protective layer. Surface regions of the nanoelement, to which catalyst material clusters can be applied, can be uncovered in a defined manner by covering a partial region of the first nanoelement with a protective layer of this type, for example using a lithography process and an etching process. If the protective layer is then removed, catalyst material spots remain only at the predetermined surface regions of the first nanoelement. As a result, second nanoelements are grown only on surface regions which were previously not covered by the protective layer and which are covered by catalyst material spots. This allows particularly good spatial definition of those regions on the first nanoelement on which a second nanoelement can be grown. It is also possible for the protective layer only to be removed after the at least one second nanoelement has been grown on.

The protective layer used may, for example, be resist, for example a photoresist, a surfactant, another organic material, an oxidized material or a metal which has no catalytic action for the growth of nanoelements, for example gold material.

The catalyst material used may, for example, be iron, cobalt or nickel, a combination of the said metals or other 3d transition metals. It is possible to use an alloy of iron and/or cobalt and/or nickel with aluminium, titanium, molybdenum and/or platinum. The said materials can advantageously be used as catalyst material, in particular if the nanoelement used is a carbon nanotube.



The following text describes the nanoelement arrangement according to the invention in more detail. Refinements of the process for producing the nanoelement arrangement also apply to the nanoelement arrangement, and vice-versa.

With the nanoelement arrangement according to the invention, it is possible for  
5 only part of the first nanoelement to be covered with catalyst material for catalyzing the growth of nanoelements. As a result of another partial region of the first nanoelement being free of catalyst material of this nature, it is possible to predetermine in a targeted manner those locations on which a second nanoelement can be grown.

10 The first nanoelement can be grown in a pore introduced in a substrate. In this way it is possible, for example, for the first nanoelement to be formed as a vertical nanoelement which extends along a preferably vertical pore introduced in a substrate. If the first nanoelement projects out of the pore and a spot of catalyst material is formed at the projecting region of the nanoelement, it is possible for a second  
15 nanoelement to be grown on the first nanoelement.

The first nanoelement may be grown in the pore on a metallization plane in the substrate. In this way, it is possible for the first nanoelement to already be electrically coupled to a metallization plane, and in this case the metallization plane can in turn be coupled to an integrated circuit in the substrate or may form part of this circuit. Since  
20 the first nanoelement and/or the second nanoelement is preferably electrically conductive or semiconducting, it is possible to create a continuous, electrically conductive connection between the integrated circuit and the first or second

nanoelement. This is advantageous with a view to forming an integrated circuit with a dimension in the nanometre range.

The first and/or the at least one second nanoelement and/or at least one additional nanoelement may be grown on top of one another and/or next to one another. In this way, it is possible to produce an areal or three-dimensional arrangement of nanoelements, so that it is clearly possible to form a network of interconnects which is suitable for numerous applications (for example memory cell circuits or logic circuits).

The first and/or the at least one second nanoelement may include a nanotube, a bundle of nanotubes or a nanorod. The nanorod may, for example, include silicon, germanium, indium phosphide, gallium nitride, gallium arsenide, zirconium oxide and/or a metal. The nanotube may, for example, be a carbon nanotube, a carbon-boron nanotube, a carbon-nitrogen nanotube, a tungsten sulphide nanotube or a chalcogenide nanotube.

The first and/or the at least one second nanoelement may, for example, be a carbon nanotube. In this case, iron, cobalt and/or nickel are preferred for use as catalyst material. It is also possible to use an alloy of iron and/or cobalt and/or nickel with aluminium, titanium, molybdenum and/or platinum.

The nanoelement arrangement of the invention may include an integrated circuit which is coupled to the first and/or the at least one second nanoelement. Therefore, the nanoelements may be connected to an integrated circuit, for example in order to couple the integrated circuit to miniaturized components.

Furthermore, in the nanoelement arrangement the nanoelements may form a multiply branched network. In other words, the nanoelements which are coupled to one another may be branched a plurality or multiplicity of times with any desired complexity, for example in order to form a desired network of electrical lines.

5 Evidently, according to the invention carbon nanotubes which have already been finally produced can be activated with a catalytically active metal suspension in such a manner that additional nanotubes can be branched from the particles of the metal suspension. In this case, it is possible for carbon nanotubes which have already been formed to be activated either along their entire length or only along a limited  
10 section, by the remaining region being covered using a resist, an oxide layer or a catalytically substantially inactive metal.

If vias (i.e., contact holes between different metallization planes in a substrate) are filled with carbon nanotubes, the process according to the invention can be used to increase the filling density of the vias with carbon nanotubes. For this purpose, by  
15 way of example, the via can be filled with a first carbon nanotube which is sheathed with a catalyst material, and then second carbon nanotube can be formed on the catalyst material on the first carbon nanotube in order to increase the filling density of the via.

According to the invention, metal clusters of a suitable size and reactivity are  
20 bonded to first carbon nanotubes, which have already been formed, and are then subjected to a further synthesis step. This synthesis step can be carried out, for example, in a furnace into which acetylene, ethene or methane is introduced under

reduced or atmospheric pressure at 300°C to 1000°C. A CVD process is suitable for forming the second nanoelements.

The metal clusters which form the catalyst material may, for example, be produced using the processes described in Cheung et al., Murray et al.

5 By way of example, it is possible to use multi-walled carbon nanotubes as first nanoelements. These can be produced using a CVD process. The carbon nanotubes produced can be used directly or may be oxidized in order to improve the solubility with a suitable chemical (for example sodium hypochlorite NaOCl). The carbon nanotubes can be treated with a suspension of iron clusters in toluene at room  
10 temperature. The iron clusters can be produced from iron pentacarbonyl ( $\text{Fe}(\text{CO})_5$ ) and oleic acid ((Z)- or cis-9-octadecenoic acid,  $\text{C}_{18}\text{H}_{34}\text{O}_2$ ). The carbon nanotube material which is in suspension can be filtered off and solvent residues can be removed. It can be resuspended using dimethylformamide ( $\text{C}_3\text{H}_7\text{NO}$ ). A drop of this solution can be applied to a substrate, or a solution which has been diluted with  
15 isopropanol can be sprayed on. During this process step, part of the substrate can be covered in order for a subsequent lift-off patterning process to be carried out, for example by means of photoresist. In this way, it is possible to ensure that carbon nanotubes are applied only to desired surface regions of a substrate. After the solution has been applied and after a possible subsequent lift-off process for removal of the  
20 photoresist, the substrate can be introduced into a reaction furnace after it has been dried. Subsequently, second carbon nanotubes can be synthesized branching off from the first carbon nanotube. Then, in order to improve the electrical contact resistance at

a respective branching point, a preferably wet-chemical, electroless nickel plating step can be carried out at the branching point.

It should be noted that according to the invention the catalyst material used may be not only metal clusters from 3d elements, such as iron, cobalt or nickel, which have been produced from the corresponding carbonyls, but also, for example, those clusters which can be produced from salts of organic acids with the aid of diols as reducing agent. Alloys of the abovementioned metals with Al, Ti, Mo, Pd, Pt, Ru, Ph, Os or Ir are also possible.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

Exemplary embodiments of the invention are illustrated in the figures and are explained in more detail in the text which follows. In the drawing:

Figures 1A and 1B show diagrammatic views of suspensions during a process for producing first carbon nanotubes covered with catalyst material clusters using a process for producing a nanoelement arrangement according to a preferred exemplary embodiment of the invention,

Figures 2A and 2B show cross-sectional views of layer sequences during the process for producing a nanoelement arrangement according to the preferred exemplary embodiment of the invention,

Figure 2C shows a cross-sectional view through a nanoelement arrangement in accordance with the preferred exemplary embodiment of the invention,

Figures 3A to 3C show electron microscope images of nanoelement arrangements in accordance with preferred exemplary embodiments of the invention.

Identical or similar components in different figures are provided with identical reference numerals.

The illustrations in the figures are diagrammatic and not to scale.

## **DETAILED DESCRIPTION OF THE PREFERRED MODE OF THE**

### **INVENTION**

The text which follows describes, with reference to Fig. 1A, Fig. 1B, Fig. 2A to Fig. 2C, a process for producing a carbon nanotube arrangement in accordance with a preferred exemplary embodiment of the invention.

Fig. 1A shows a container 100 which contains a suspension of toluene solvent 101 and iron clusters 102. The iron clusters are surrounded by a thin film of oleic acid (not shown).

Fig. 1B shows the operating state of the container 100 after carbon nanotubes 110 have been introduced into the suspension using a CVD process. The carbon nanotubes 110 are surrounded along most of their length with a protective layer (not shown) of a photoresist, and the carbon nanotubes 110 are only free of the protective layer in a region surrounding an end section of the carbon nanotubes 110. After the carbon nanotubes 110 partially covered with the protective layer have been introduced into the suspension of toluene 101 and iron clusters 102, iron clusters 102 attach themselves only to those locations of the carbon nanotubes 110 at which the latter are free of the protective layer. The oleic acid sheath by which the iron clusters 102 are surrounded evidently serves as a bonding layer for bonding the iron clusters 102 to the carbon nanotubes 110. This makes it possible for iron clusters 102 to be attached only

to spatially defined locations on the carbon nanotubes, as catalyst material spots for catalyzing subsequent formation of second carbon nanotubes.

In a further process step, the complexes of iron clusters 102 and carbon nanotubes 110 are separated from the solvent 101 and resuspended in  
5 dimethylformamide 201.

The text which follows describes, with reference to the layer sequences shown in Fig. 2A to 2C, how a carbon nanotube arrangement according to a preferred exemplary embodiment of the invention is produced using the resuspended carbon nanotubes 110 provided with iron clusters 102.

10 The layer sequence 200 shown in Fig. 2A is formed from a silicon substrate 202, in which an integrated circuit 203 is formed. An electrically conductive coupling means 204 is formed in a contact hole in the silicon substrate 202. A photoresist layer 205 is applied to the surface of the silicon substrate 202 and etched together with the silicon substrate 202 to form the contact hole using a lithography process and an  
15 etching process. The photoresist layer 205 is selected from a material which is such that carbon nanotubes do not attach themselves or scarcely attach themselves to this material. A drop of the suspension of dimethylformamide 201 and the carbon nanotube 110 provided with the iron cluster 102 is applied to the contact hole in the layer sequence 200 by means of a micropipette. The carbon nanotube 110 is oriented  
20 vertically in the contact hole and is bonded to the electrically conductive coupling means 204 in order to be coupled to the integrated circuit 303.

To obtain the layer sequence 210 shown in Fig. 2B, the dimethylformamide material 201 is removed by drying. Furthermore, the material of the photoresist layer

205 is removed using a suitable etching process. The etching process is a selective etching process which is selected in such a manner that the etching removes the photoresist layer 205 but not the carbon nanotube 110 together with the catalyst material spot 102.

5 To obtain the carbon nanotube arrangement 220 in accordance with the preferred exemplary embodiment of the invention shown in Fig. 2C, the layer sequence 210 is subjected to a CVD (chemical vapour deposition) process step in a reaction furnace by acetylene material under reduced pressure being introduced into the process chamber at 700°C. As a result, additional carbon nanotubes 221 are  
10 formed starting from the iron cluster 102 as catalyst material spot. This results in a spatially defined branching of carbon nanotubes.

The text which follows describes, with reference to Fig. 3A to Fig. 3C, electron microscope images of carbon nanotube arrangements in accordance with preferred exemplary embodiments of the invention.

15 The electron microscope image 300 from Fig. 3A shows a primary carbon nanotube 301, on which a catalyst material spot 302 is formed. A branching of secondary carbon nanotubes 303 starting from this catalyst material spot 302 made from iron material can be seen.

Fig. 3B illustrates an electron microscope image 310 with a particularly high  
20 magnification factor, showing a primary carbon nanotube 311. Secondary carbon nanotubes 323 are shown starting from catalyst material spots 312 on the primary carbon nanotube 321.



Fig. 3C shows yet another electron microscope image 320, in which a secondary carbon nanotube 323 has been grown starting from a catalyst material spot 322 on a primary carbon nanotube 321.